

-Supporting Information-
Time-Resolved Optical-Pump, Resonant X-ray Probe
Spectroscopy of 4-Thiouracil; a Simulation Study

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Contents

Contents	S2
1 Loop Diagram Rules	S3
2 Supplementary Figures	S4

1 Loop Diagram Rules

The loop diagram of the optical pump - resonant X-ray probe signal is shown in Scheme 1b in the main manuscript and Figure S6. The Diagram rules are as follows:

- Time runs along the loop clockwise from bottom left to bottom right.
- Each field interaction is represented by an arrow, which either points to the right (photon annihilation and excitation of the molecule) or to the left (photon creation and de-excitation of the molecule).
- Free evolution periods on the left branch indicate forward propagation in real time, and on the right branch to backward propagation respectively.
- The last field interaction is the detected photon mode. In addition, the gray bar represents the period of free evolution.

2 Supplementary Figures

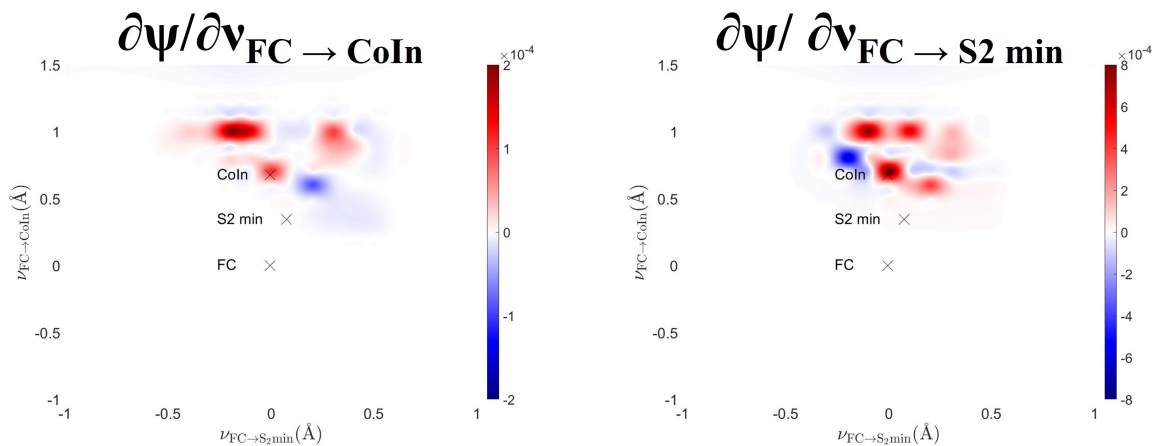


Figure S 1: Nonadiabatic couplings versus the two nuclear coordinates of the 4-thiouracil. The location of the FC, CoIn, and S2 min are marked with X. The spiky nature due to the phase change across the CoIn is observed.

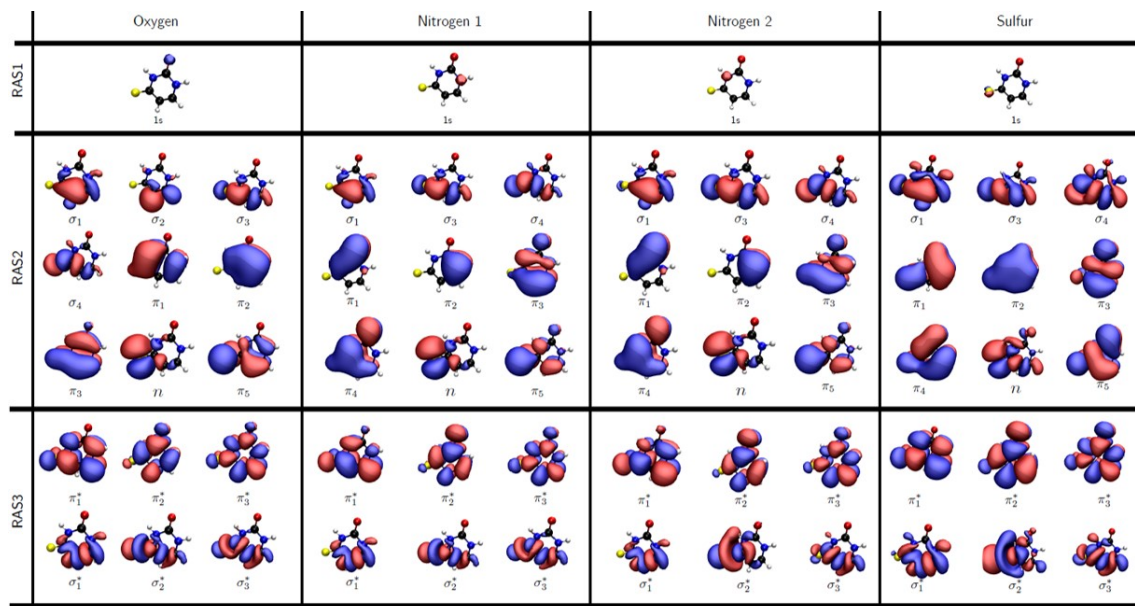


Figure S 2: CASSCF(20,16) active space. Active space for 4-thiouracil at the optimized ground state at the MP2 level (20 electrons in 16 orbitals) averaged over 3 lowest valence states, $S_0 - S_2$ and 30 core states for each sulfur and 10 core states for oxygen and nitrogen K-edges.

Figure S 3: The nuclear wavepacket molecular dynamics movie on S_2 , S_1 , and S_0 PES. S_2 wavepacket (gray contours), S_1 wavepacket (pink contour), and S_0 wavepacket (black contour). The location of the FC, S_2 min, and CoIn is marked with "X". The pump-probe time-delay and the populations are shown in the bottom left corner. see the attached movie

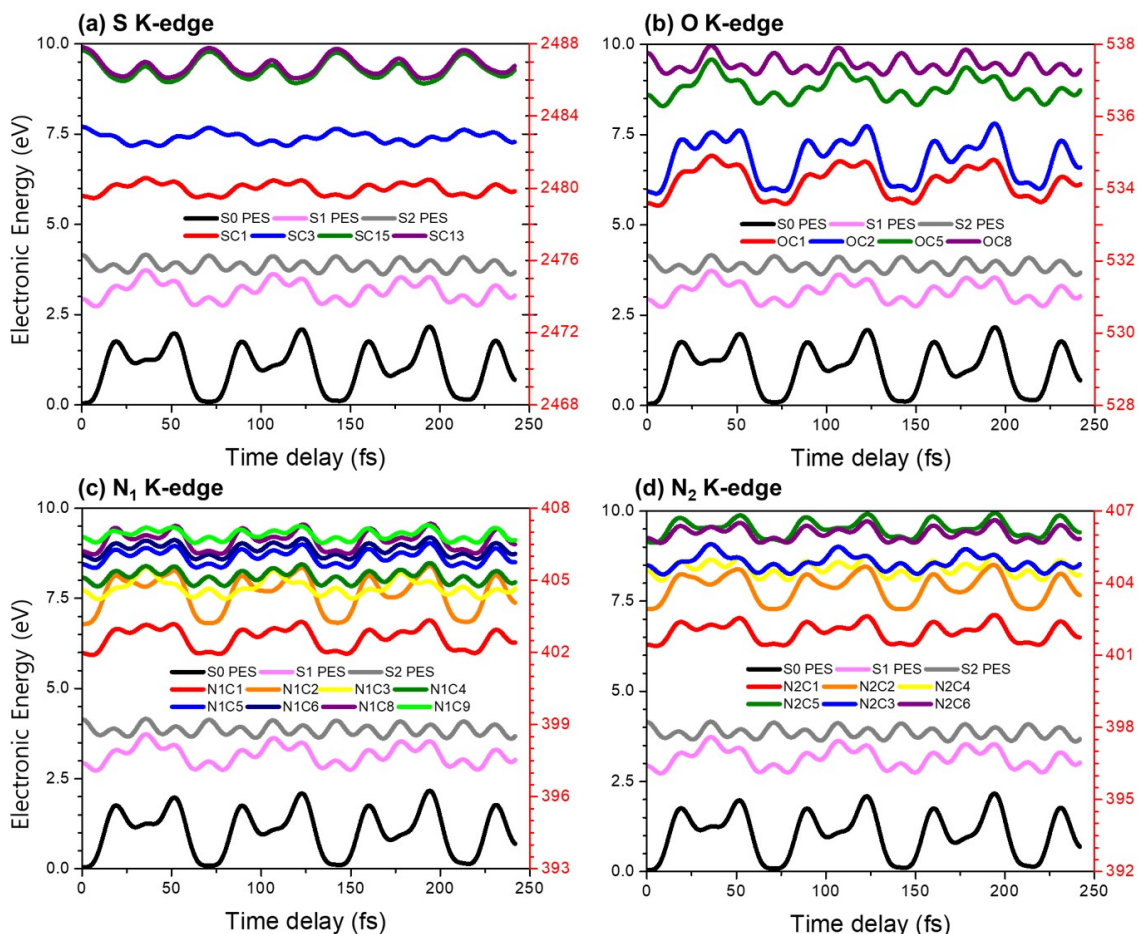
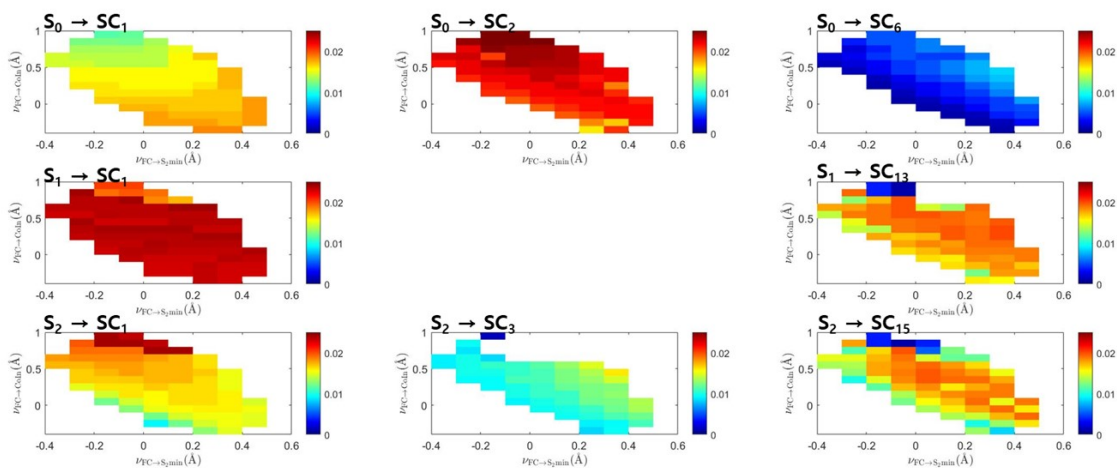


Figure S 4: Time-evolving electronic states levels for (a) S, (b) O, (c) N_1 , and (d) N_2 K-edges. The valence states, S_0 , S_1 , and S_2 are shown in black, pink, and gray lines, respectively. See the left y-axis for the valence energy levels and the right y-axis for the core energy levels.

(a) S K-edge



(b) O K-edge

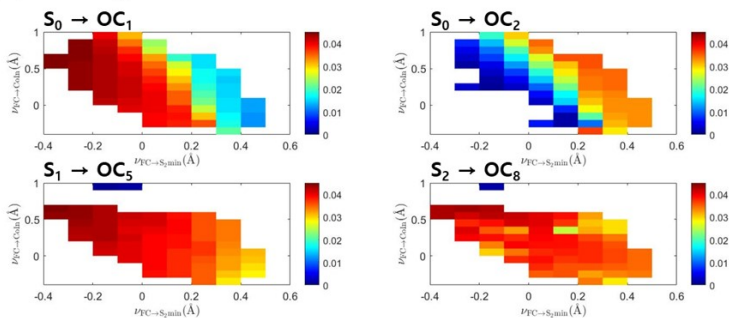


Figure S 5: Transition dipole moment between valence (S_0 , S_1 , and S_2) and core states over two-dimensional nuclear grids. (a) sulfur, (b) oxygen, and (c) nitrogen K-edges. Profiles pertaining to the same heteroatom are plotted in the same [min:max] range to allow easier comparison.

(c) N K-edge

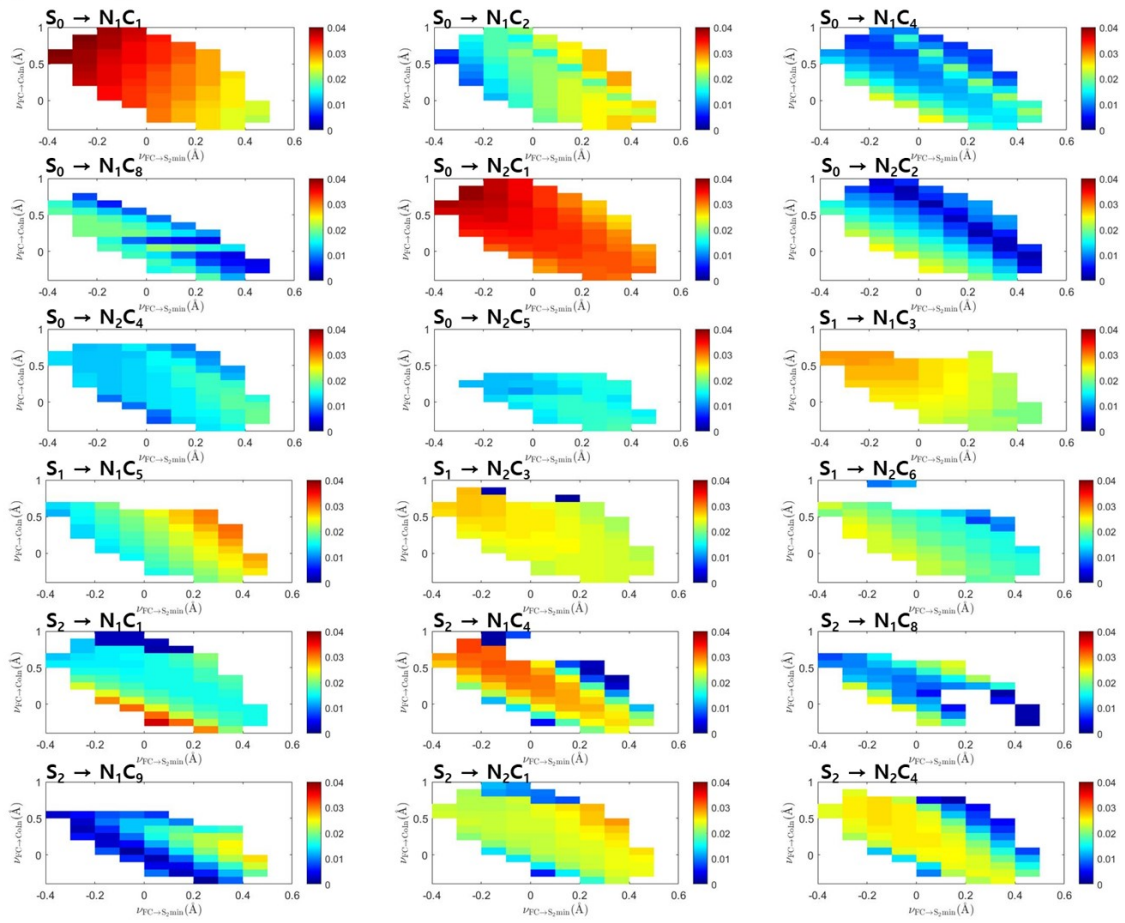


Figure S 5: (continued)

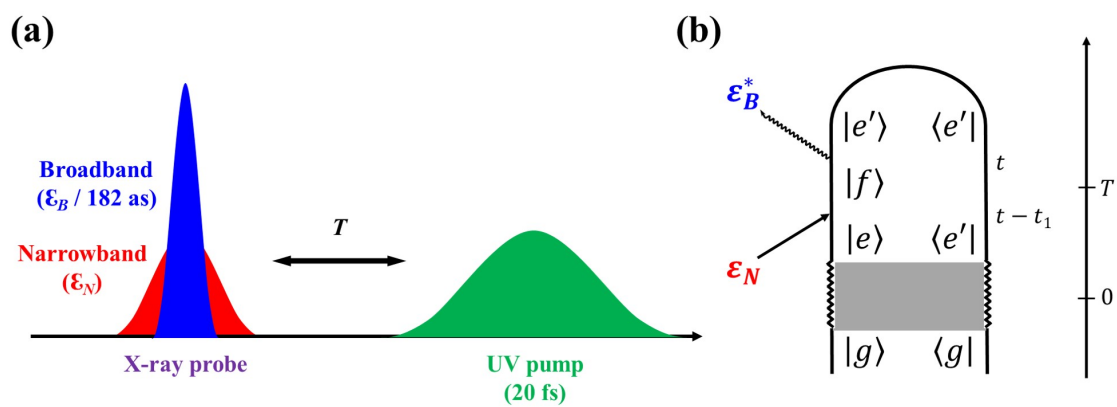


Figure S 6: (a) Pulse configuration for X-ray narrowband/broadband hybrid probe pulse and (b) the relevant Loop diagram. A hybrid X-ray field \mathcal{E}_B (broad) and \mathcal{E}_N (narrow) is used instead of a single broadband pulse that interacts twice. An incoming X-ray pulse (\mathcal{E}_N) excites a molecule on a valence electronic surface $|e\rangle$ into a core level $|f\rangle$ after time delay T following an initial excitation into a non-stationary state and free evolution period (gray box). The signal field emission is stimulated by a broadband attosecond X-ray pulse (\mathcal{E}_B).